Preventing or Extinguishing Molten Sulfur Tank and Pit Fires

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Trimeric Background & Questions Policy

- Trimeric Corporation
  - 18 regular staff ChEs & 6 Senior Assoc. ChEs
  - Specialized = Process Chemical Engineers
  - Generalized = Experience Across Industries and Processes
  - Depth of Experience in Sulfur Applications
    - Design and troubleshooting of molten sulfur tanks, loading, vent systems
    - See previous Brimstone papers for examples
- Written technical paper for this topic available upon request
- Questions policy

Topics

- Introduction and Background
- Fire and Explosion Hazards
- Fire Prevention and Detection Techniques
- Fire Suppression Techniques
- Conclusions

Introduction:
Can I Just Follow Standards?

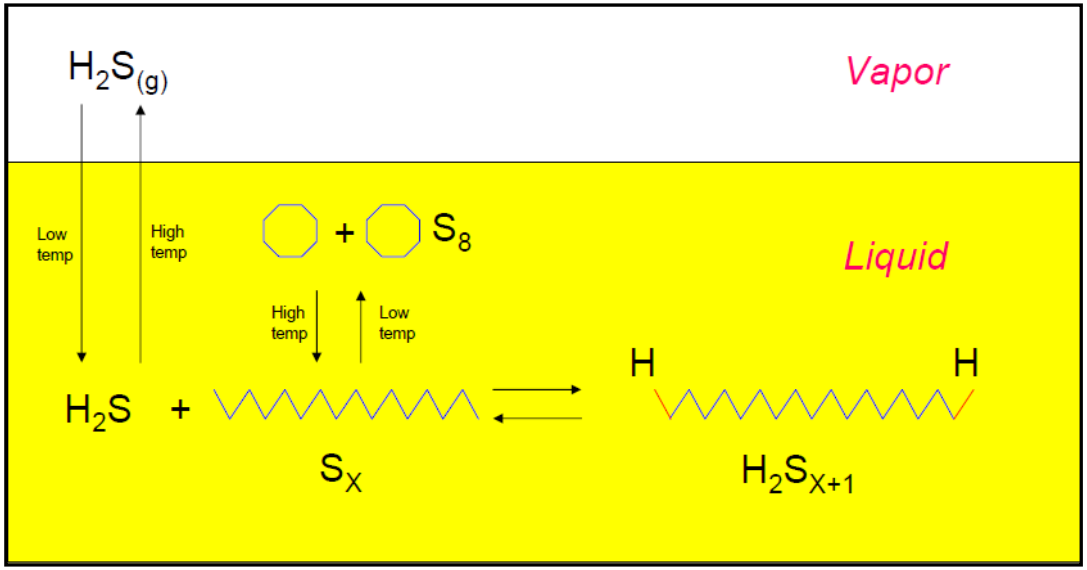
- NFPA-655: Standard for Prevention of Sulfur Fires and Explosions

- Two Scenarios:
  - Required/choose to follow standard
    - Standards are not fully prescriptive:
      - Example: Rapid sealing of tanks and pits
  - Cannot practically comply with standard
    - Standards do not always provide flexibility:
      - Example: Less steam available for snuffing/sealing than in standard

- **GOAL: Use knowledge and field experience to fill in the gaps around standards**

Introduction: Chemistry

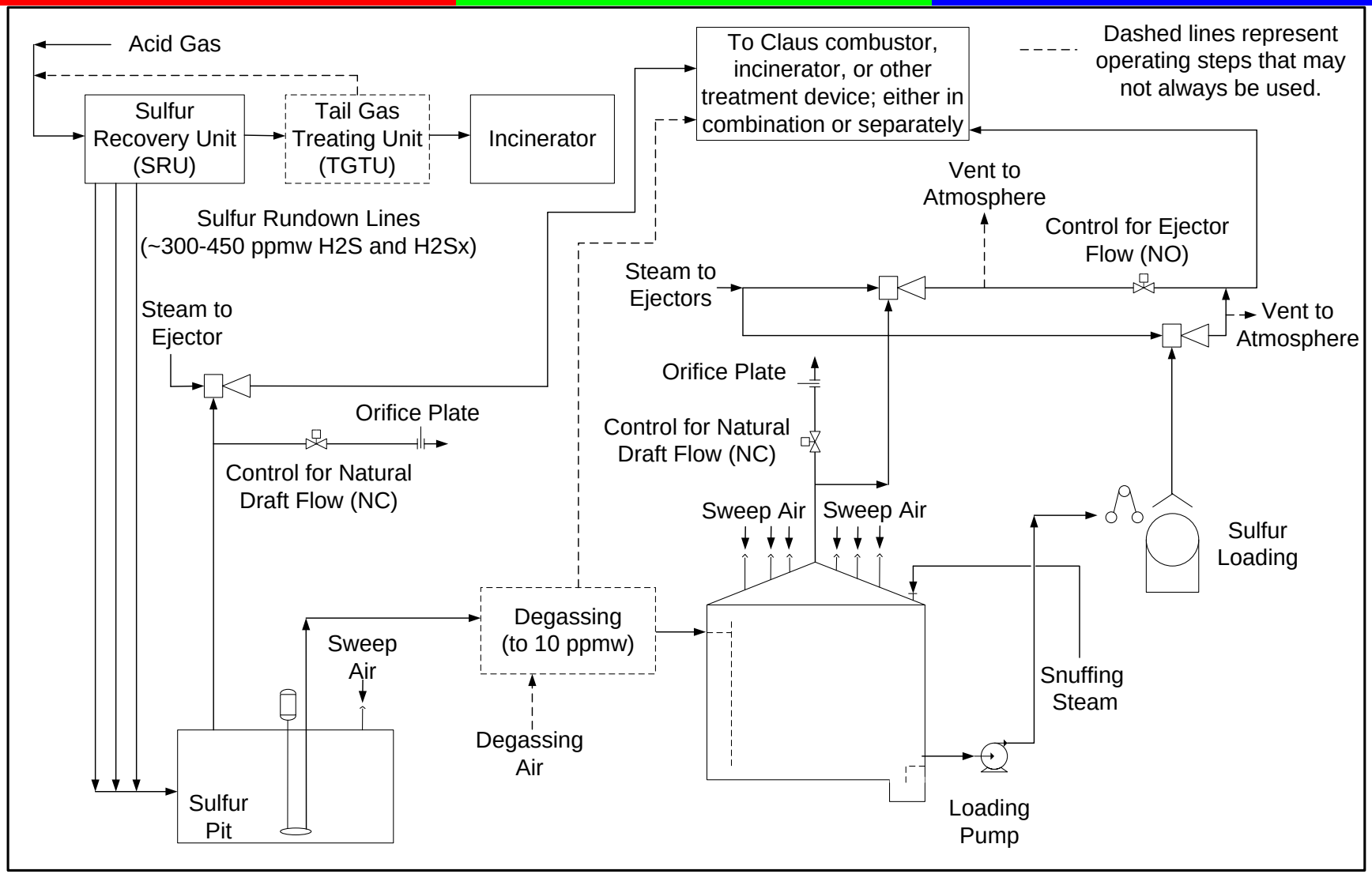
- Claus SRU "Sulfur"



Source: 2007 LRGCC Fundamentals

- Other Volatile/Vapor Components : SO_2, S_6/S_8, & sulfur mist
- Molten sulfur will burn
- **Fuel for fires**

Molten Sulfur Storage and Handling System



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Molten Sulfur Tank Rupture

Source: Sulfur Recovery Fundamentals, 2007 LRGCC, Hatcher, Nassato, Chow, Huffmaster

Fire Hazards: Fire Triangle in Sulfur Handling

- Fuel (components that will burn)
  - H_2S (**Next Slide**)
  - Molten sulfur liquid
  - Sulfur particulate (solid or liquid)
- Ignition Source
  - Static discharge (Free-falling sulfur)
  - Hot surfaces in equipment (e.g., pump bearing)
  - Improper operating temperature (**Following Slides**)
  - Pyrophoric iron sulfide (**Following Slides**)
- Oxygen
  - Air present by design (tank/pit vented to atmosphere)
  - Air present off-design (leaks, maintenance, etc.)

Fire Hazards: LEL of H_2S

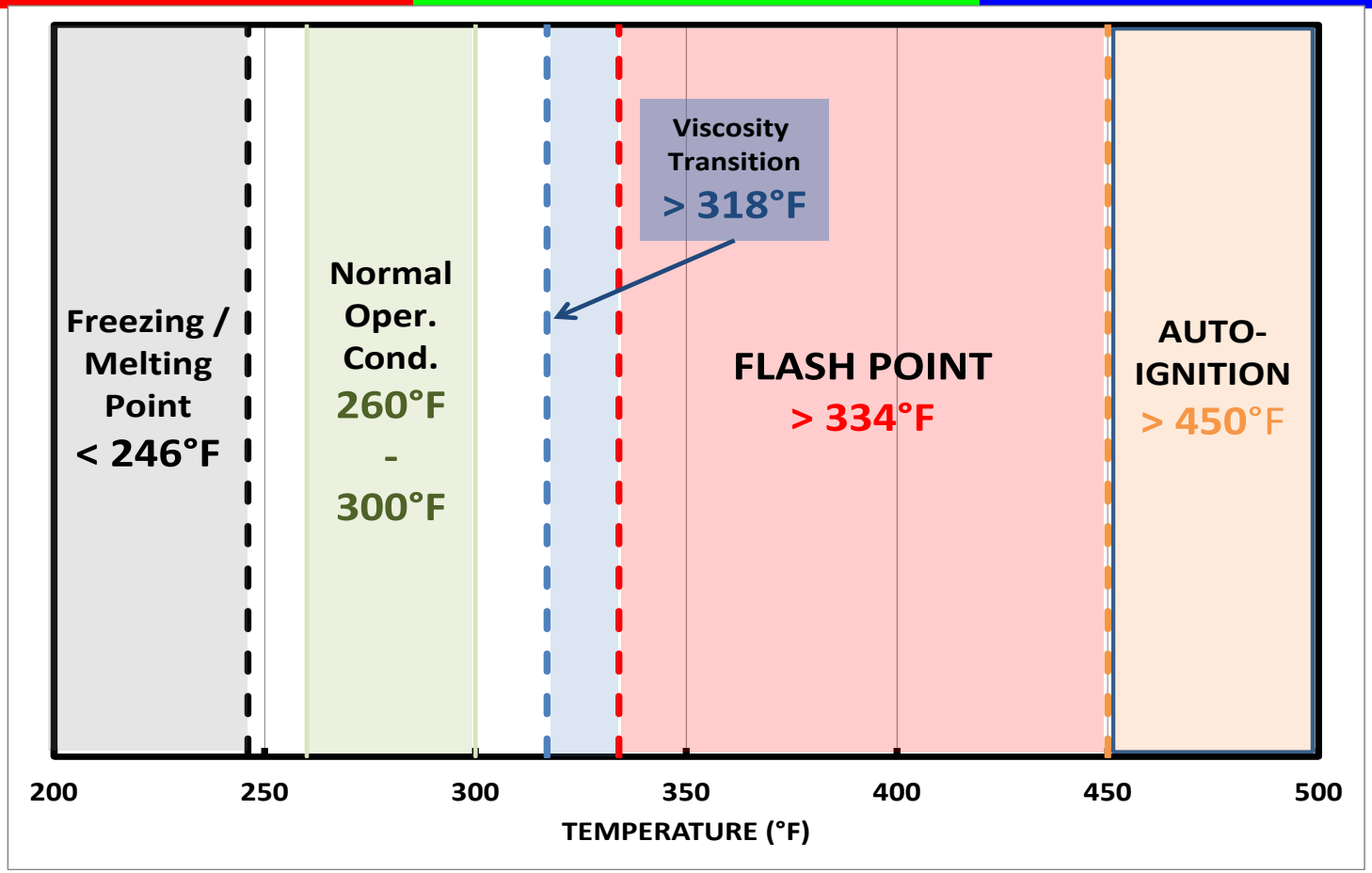
- H_2S is flammable
- LEL for H_2S (3 vol % H_2S @ 330°F[1])
- If vapor headspace (e.g., tank) is <u>stagnant</u>:

Total H_2S in Sulfur	Temperature	H_2S in Vapor Space	Notes
ppmw H_2S +H_2S_x	F	vol%	
300	300	29.7	> LEL for H_2S
300	280	40.5	> LEL for H_2S
150	300	14	> LEL for H_2S
150	280	20.4	> LEL for H_2S
50	300	4.3	> LEL for H_2S
50	280	6.9	> LEL for H_2S
10	300	0.7	Degassed Sulfur. Lethal H_2S levels.
10	280	1.4	Degassed Sulfur, > 25% of LEL of H_2S

Source: 2000 LRGCC Fundamentals

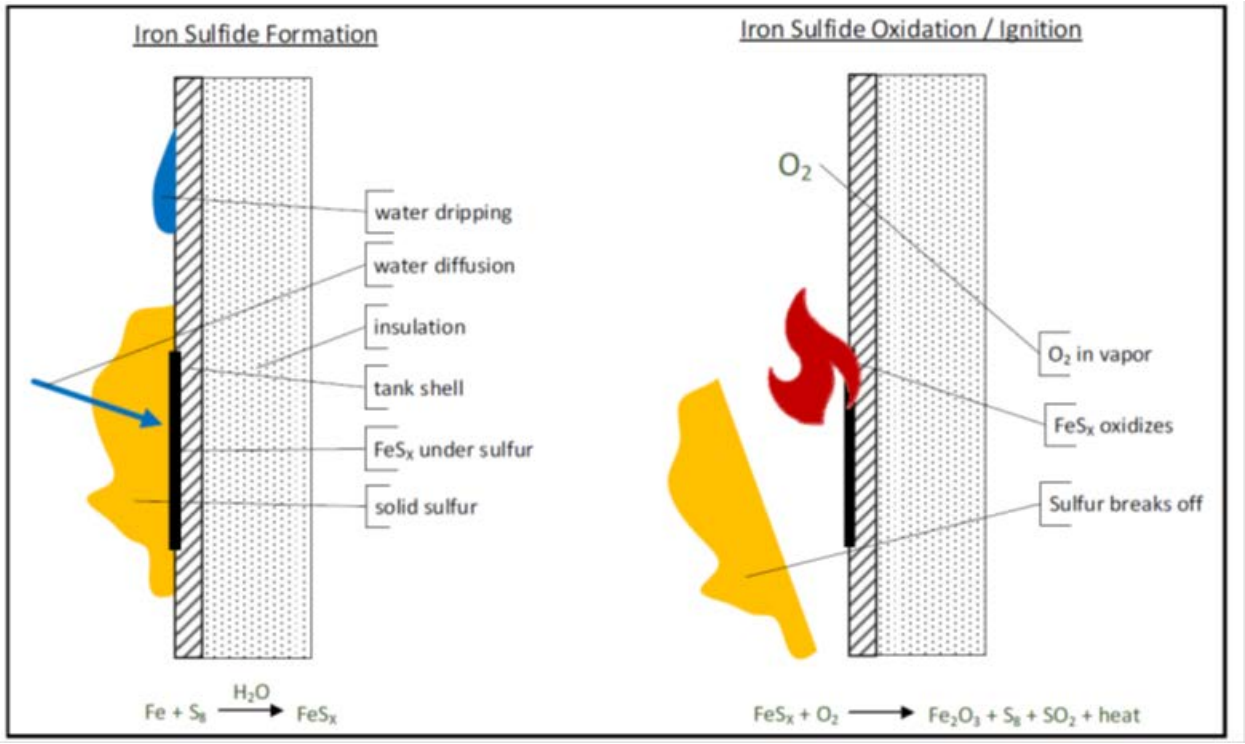
1: Conventional LEL for H_2S is 3.4 vol% at 330 F. Values updated by studies using new methods (e.g., Pahl & Holtappels 2005).

Molten Sulfur Operating Temperature



- NFPA-655: Normal Handling Temp = 246°F - 309°F

Pyrophoric Iron Sulfide



Source: Forbes & Cipriano (CSI/Ametek), Brimstone 2018

- Reducing environment necessary for FeS formation
- Oxidizing environment necessary for FeS ignition
- Known cause of tank explosions and fires (in literature and Trimeric's knowledge)

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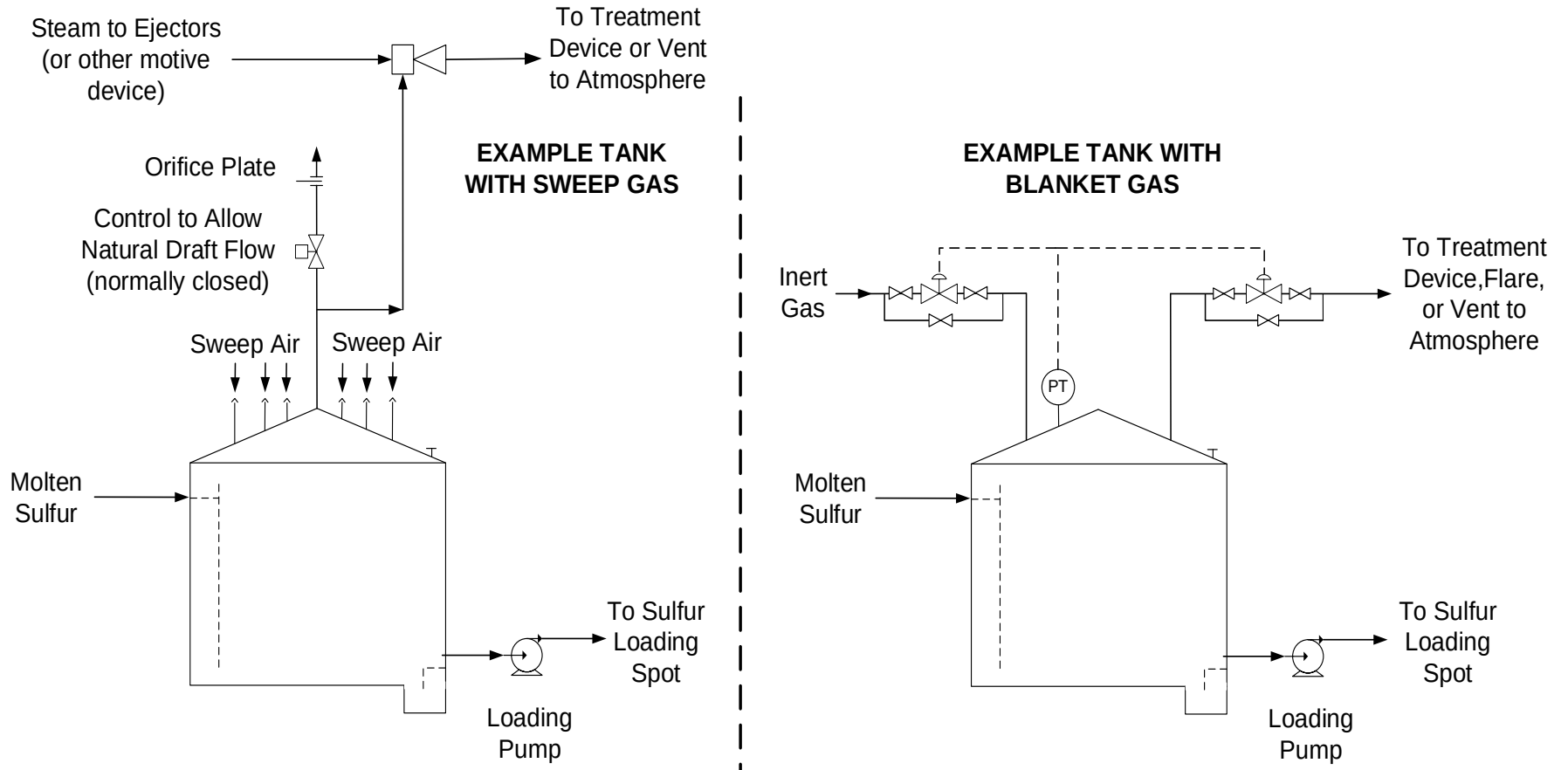
Fire Prevention: Sweeping vs. Blanketing



Approach 1 - Minimize Combustible Gas Concentration: Sweep Gas

- Goal: Dilute headspace vapor to manage H_2S concentration (e.g., < 25% of LEL)
  - Details of sweep design covered elsewhere[1]
- Air is best practice, but others used (N_2, steam, fuel gas etc.)
- Sweep gas must be vented or managed - critical design consideration[2]

1: K. E. McIntush, K. Fisher, D. Sachde and C. A. M. Beitler, "Design Considerations for Natural Draft Ventilation in Molten Sulfur Storage Tanks," in *Brimstone Sulfur Symposium*, Vail, CO, 2018.

2: K. E. McIntush, D. Sachde and C. A. M. Beitler, "Molten Sulfur Vent Stream Disposition - Vent Stream Routing, Managing Emissions, and Impact of Process Conditions/Equipment," in *Brimstone Sulfur Recovery Symposium*, Vail, Colorado, 2019.

Approach 2 – Minimize/Manage Oxidant Concentration: Blanket Gas

- Goal: Exclude air to keep O_2 below the limiting oxygen concertation (LOC).
  - Details of blanket gas design covered elsewhere[1]
- N_2 is common but other gases may be used (CO_2)
- Pyrophoric FeS accumulation - critical design consideration
- Special Case: Inert gas with O_2 (below LOC)
  - Limit/prevent FeS accumulation
  - Combustion exhaust/flue gas blanketing
    - Known successful application to molten sulfur tank
    - Has been used in transport industry for various cargo
  - Inert with O_2 for blanketing reported in SRU/other equipment

1: D. Sachde, C. Beitler, K. McIntush and K. Fisher, "Preventing explosions in molten sulphur tanks (in press)," Sulphur Magazine, 2020

Sweep and Blanket Gas Selection

	Air	Inert Gas (e.g., N_2)	Inert with O_2
Use	Sweep	Sweep or Blanket	Sweep or Blanket
Flammability	Introduces oxygen, creates risk for ignition.	No air present.	Introduces oxygen at low concentration (below the LOC).
Explosion Risk	Adequate sweep air should mitigate risk.	FeS formation in reducing environment. **Exposure to Air = Pyrophoric**	Proper O_2 concentration can limit or eliminate FeS accumulation.
Tank Pressure	**Slight vacuum**	**Slight positive pressure to exclude air.**	**Slight positive pressure to exclude air.**
Cost	Readily available. Some cost may be required for heating.	Tie into existing system or add new source of inert gas.	Tie into existing system (e.g., flue/exhaust gas) or add new source of inert gas, both with appropriate oxygen content.

Fire Detection Methods

- Molten sulfur fire focus (as opposed to vapor)
- Detection:
  - Air Flow Measurement
    - Prevention – early detection of insufficient sweep air
  - Temperature Measurements
    - Multiple points: headspace & vent line (e.g., ejector suction)
    - Rate of change: 2 – 5 °F/min headspace temp
  - SO_2 Detection/Monitoring
    - Large increase over baseline
  - Visual Detection
    - Reports of yellow plumes during fires

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Fire Suppression: Sealing/Snuffing Steam

- Sealing Steam
  - 1 lb/min/100 ft^3 tank volume (NFPA-655)
  - Positive pressure = seal tank to prevent air ingress
- Snuffing Steam
  - 2.5 lb/min/100 ft^3 tank volume (NFPA-655)
  - Displace air/O_2 at fuel/fire interface + sealing
  - Large tank/pit = large steam volume = overpressure risk[1]
- Prior to 2017 NFPA-655: Snuffing Steam Only
- Industry – Lower steam rates successfully applied
- Design Considerations
  - Valve location & dry steam verification
  - Prevent plugging
  - Verify “sealing”
  - Verify overpressure risk
  - Time to activation: 5 – 10 minutes (industry experience)

1: A. D. Mosher, S. M. McGuffie and D. H. Martens, "Molten Sulfur Fire Sealing Steam Requirements: Proposed Modifications to NFPA 655," in Brimstone Sulfur Symposium, Vail, CO, 2015.

Fire Suppression: Mechanical Sealing

- NFPA-655: “Rapid sealing of the enclosure to exclude air”
- Mechanical sealing – Close all intakes/vents
- Example Tank: Tank Heat-up analysis
  - Fire dynamics complex
  - Simplifying assumptions:
    - Fire until O_2 below LOC
    - Fast combustion case: heat transfer to headspace only
    - Slow combustion case: heat transfer to entire tank + contents
  - Fast Combustion: $\Delta T > 1{,}500°F$, $\Delta P = > +30$ psi (w/o relief)
  - Slow Combustion: $\Delta T \sim 10°F$, $\Delta P = \sim 0.1$ psi (w/o relief)
- Conclusion: Overpressure, vacuum relief needed
- Field Operation: Tanks have experienced roof collapse/overpressure. Relief devices may fail (plugging). Extreme care required.

Fire Suppression: Other

- Water Mist
  - NFPA-655: Open Containers
  - Industry: Used successfully (merchant sulfur vessels, molten sulfur tanks)
  - **Must be** fine mist (not spray or large droplets)
  - Can serve dual function of sealing (mist forms steam)
  - Limited engineering guidance in literature (experience and judgment needed)

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Conclusions

- Molten sulfur storage applications:
  - Flammable components (H_2S, sulfur)
  - Ignition Sources (Static discharge, elevated T, pyrophoric FeS)
  - Air (oxidant)
- Fire Prevention Methods: Eliminate Components of Fire Triangle
  - Sweep gas to dilute H2S (Handle vent gas)
  - Blanketing to minimizing O2 (Pyrophoric FeS formation)
  - Design/operation to avoid ignition sources
- Fire Detection: Identify early signs of fire
  - Reduced air flow (preventative)
  - Temperature, SO_2 changes
  - Yellow plume from vent
- Fire Suppression: Prevent air from feeding fire or extinguish fire
  - Snuffing vs. Sealing Steam (steam requirements)
  - Mechanical Sealing (overpressure, vacuum, heat-up)
  - Water Mist (Fine mist required, least information)
- Optimal approach to be evaluated on site-by-site basis

Questions?

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- Publications:
  - www.trimeric.com/publications
- Reminder: Technical paper associated with this presentation covers additional topics and details - available upon request